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CONDUCTIVE COMPOSITION AND FLEXIBLE CONDUCTIVE MATERIAL

[Dodensei Soseibutsu oyobi Junansei Dodentai]

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[Claims]

[Claim 1] A conductive composition, which comprises a water-soluble conductive polymer (A) having a sulfonic acid group and/or a carboxyl group, a vinyl polymer emulsion (B) with a glass transition temperature of 40°C or below and a solvent (C).

[Claim 2] The conductive composition according to Claim 1, wherein the conductive composition contains a surfactant (D).

[Claim 3] The conductive composition according to Claim 1 or 2, wherein the conductive composition contains a polyvinyl alcohol (E).

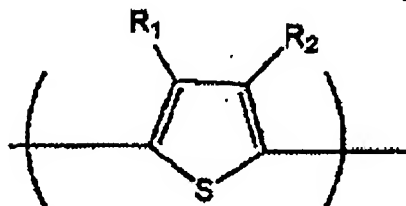
[Claim 4] The conductive composition according to any of Claims 1 ~ 3, wherein the vinyl polymer emulsion (B) with a glass transition temperature of 40°C or below is an emulsion obtained by emulsion polymerization of a vinyl polymeric monomer (G) in a solvent dissolving or dispersing a vinyl polymer (F) containing an acid group with a basic compound, and the vinyl poly-

¹Numbers in the margin indicate pagination in the foreign text.

mer (F) containing an acid group is in a range of solid acid value of 50 ~ 200 mgKOH/g and a range of mass average molecular weight of 5,000 ~ 50,000.

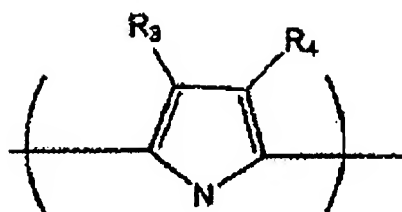
[Claim 5] The conductive composition according to any of Claims 1 ~ 4, wherein the water-soluble conductive polymer (A) contains 20 ~ 100% of at least one repeating unit selected from a set composed of

[Chem 1]



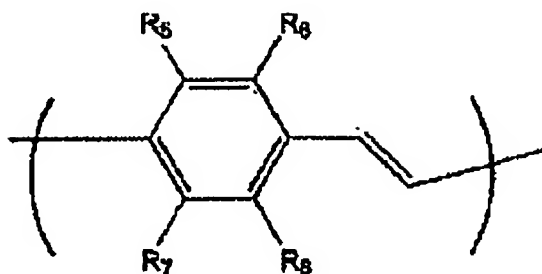
(where R_1 , R_2 are selected from a set composed of H, $-\text{SO}_3^-$, $-\text{SO}_3\text{H}$, $-\text{R}_{35}\text{SO}_3^-$, $-\text{R}_{35}\text{SO}_3\text{H}$, $-\text{OCH}_3$, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{N}(\text{R}_{35})_2$, $-\text{NHCOR}_{35}$, $-\text{OH}$, $-\text{O}^-$, $-\text{SR}_{35}$, $-\text{OR}_{35}$, $-\text{OCOR}_{35}$, $-\text{NO}_2$, $-\text{COO}^-$, $-\text{R}_{35}\text{COO}^-$, $-\text{COOH}$, $-\text{R}_{35}\text{COOH}$, $-\text{COOR}_{35}$, $-\text{COR}_{35}$, $-\text{CHO}$ and $-\text{CN}$, respectively and separately; here, R_{35} is a $\text{C}_1 \sim \text{C}_{24}$ alkyl, aryl or aralkyl or alkylene, arylene or aralkylene group, and at least one of R_1 , R_2 is a group selected from a set composed of $-\text{SO}_3^-$, $-\text{SO}_3\text{H}$, $-\text{R}_{35}\text{SO}_3^-$, $-\text{R}_{35}\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{COO}$, $-\text{R}_{35}\text{COO}^-$ and $-\text{R}_{35}\text{COOH}$.)

[Chem 2]



(where R_3 , R_4 are selected from a set composed of H, $-\text{SO}_3^-$, $-\text{SO}_3\text{H}$, $-\text{R}_{35}\text{SO}_3^-$, $-\text{R}_{35}\text{SO}_3\text{H}$, $-\text{OCH}_3$, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{N}(\text{R}_{35})_2$, $-\text{NH}-\text{COR}_{35}$, $-\text{OH}$, $-\text{O}^-$, $-\text{SR}_{35}$, $-\text{OR}_{35}$, $-\text{OCOR}_{35}$, $-\text{NO}_2$, $-\text{COO}^-$, $-\text{R}_{35}\text{COO}^-$, $-\text{COOH}$, $-\text{R}_{35}\text{COOH}$, $-\text{COOR}_{35}$, $-\text{COR}_{35}$, $-\text{CHO}$ and $-\text{CN}$, respectively and separately; here, R_{35} is a $\text{C}_1 \sim \text{C}_{24}$ alkyl, aryl or aralkyl or alkylene, arylene or aralkylene group, and at least one of R_3 , R_4 is a group selected from a set composed of $-\text{SO}_3^-$, $-\text{SO}_3\text{H}$, $-\text{R}_{35}\text{SO}_3^-$, $-\text{R}_{35}\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{COO}^-$, $-\text{R}_{35}\text{COO}^-$ and $-\text{R}_{35}\text{COOH}$.)

[Chem 3]

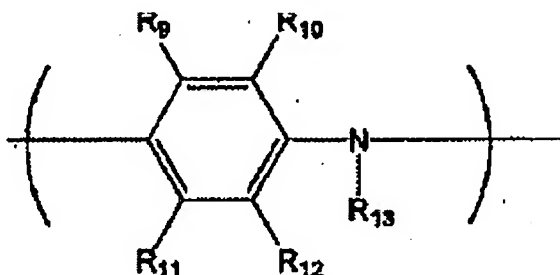


(where $R_5 \sim R_8$ are selected from a set composed of H, $-\text{SO}_3^-$, $-\text{SO}_3\text{H}$, $-\text{R}_{35}\text{SO}_3^-$, $-\text{R}_{35}\text{SO}_3\text{H}$, $-\text{OCH}_3$, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{N}(\text{R}_{35})_2$, $-\text{NH}-\text{COR}_{35}$, $-\text{OH}$, $-\text{O}^-$, $-\text{SR}_{35}$, $-\text{OR}_{35}$, $-\text{OCOR}_{35}$, $-\text{NO}_2$, $-\text{COO}^-$, $-\text{R}_{35}\text{COO}^-$, $-\text{COOH}$,

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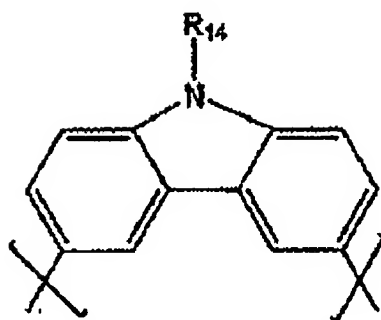
-R₃₅COOH, -COOR₃₅, -COR₃₅, -CHO and -CN, respectively and separately; here, R₃₅ is a C₁ ~ C₂₄ alkyl, aryl or aralkyl or alkylene, arylene or aralkylene group, and at least one of R₅ ~ R₈ is a group selected from a set composed of -SO₃⁻, -SO₃H, -R₃₅SO₃⁻, -R₃₅SO₃H, -COOH, -COO⁻, -R₃₅COO⁻ and -R₃₅COOH.)

[Chem 4]



(where R₉ ~ R₁₃ are selected from a set composed of H, -SO₃⁻, -SO₃H, -R₃₅SO₃⁻, -R₃₅SO₃H, -OCH₃, -CH₃, -C₂H₅, -F, -Cl, -Br, -I, -N(R₃₅)₂, -NHCOR₃₅, -OH, -O⁻, -SR₃₅, -OR₃₅, -OCOR₃₅, -NO₂, -COO⁻, -R₃₅COO⁻, -COOH, -R₃₅COOH, -COOR₃₅, -COR₃₅, -CHO and -CN, respectively and separately; here, R₃₅ is a C₁ ~ C₂₄ alkyl, aryl or aralkyl or alkylene, arylene or aralkylene group, and at least one of R₉ ~ R₁₃ is a group selected from a set composed of -SO₃⁻, -SO₃H, -R₃₅SO₃⁻, -R₃₅SO₃H, -COOH, -COO⁻, -R₃₅COO⁻ and -R₃₅COOH.)

[Chem 5]

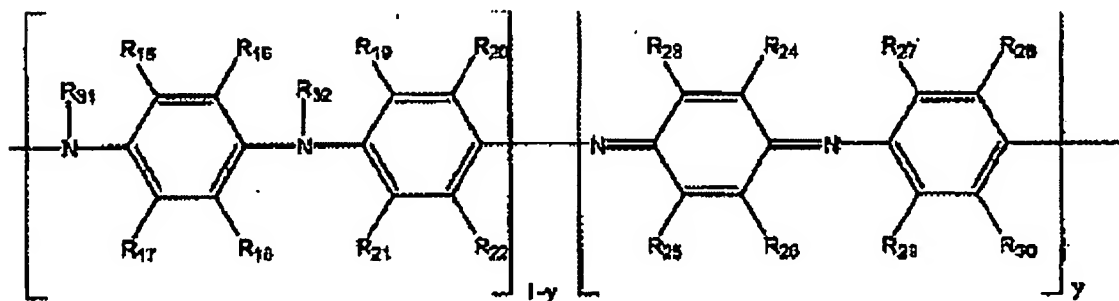


(where R_{14} is selected from a set composed of $-\text{SO}_3^-$, $-\text{SO}_3\text{H}$, $-\text{R}_{36}\text{SO}_3^-$, $-\text{R}_{36}\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{COO}^-$, $-\text{R}_{35}\text{COO}^-$, $-\text{R}_{35}\text{COOH}$; here, R_{36} is a $\text{C}_1 \sim \text{C}_{24}$ alkylene, arylene or aralkylene group.) in all repeating units of polymer and has a molecular weight of $2,000 \sim 1,000,000$.

[Claim 6] The conductive composition according to any of Claims 1 ~ 4, wherein the water-soluble conductive polymer (A) contains 20 ~ 100% of at least one repeating unit selected from a set composed of

[Chem

6]



(where y represents any number of $0 < y < 1$, $R_{15} \sim R_{32}$ are selected from a set composed of H , $-\text{SO}_3^-$, $-\text{SO}_3\text{H}$, $-\text{R}_{35}\text{SO}_3^-$, $-\text{R}_{35}\text{SO}_3\text{H}$,

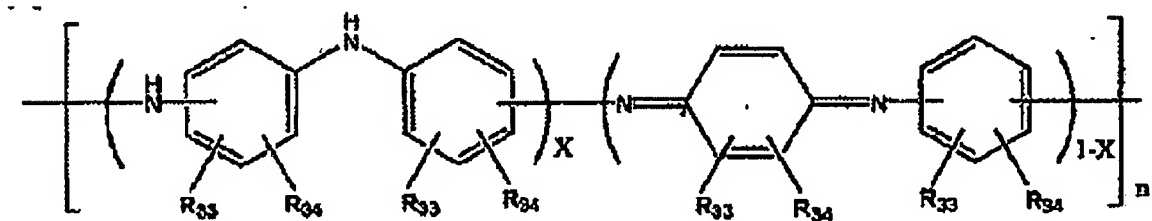
-OCH₃, -CH₃, -C₂H₅, -F, -Cl, -Br, -I, -N(R₃₅)₂, -NHCOR₃₅, -OH, -O⁻,
 -SR₃₅, -OR₃₅, -OCOR₃₅, -NO₂, -COO⁻, -R₃₅COO⁻, -COOH, -R₃₅COOH, -COOR₃₅,

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-COR₃₅, -CHO and -CN, respectively and separately; here, R₃₅ is a C₁ ~ C₂₄ alkyl, aryl or aralkyl or alkylene, arylene or aralkylene group, and at least one of R₁₅ ~ R₃₂ is a group selected from a set composed of -SO₃⁻, -SO₃H, -R₃₅SO₃⁻, -R₃₅SO₃H, -COOH, -COO⁻, -R₃₅COO⁻ and -R₃₅COOH.) in all repeating units of polymer and has a mass-average molecular weight of 2,000 ~ 1,000,000.

[Claim 7] The conductive composition according to any of Claims 1 ~ 4, wherein the water-soluble conductive polymer (A) is

[Chem 7]



(where R₃₃ represents one group selected from a set composed of a sulfonic acid group, a carboxyl group, their alkali metal salts, ammonium salts and substituted ammonium salts, R₃₄ represents one group selected from a set composed of methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, dodecyl, tetracosyl, methoxy, ethoxy, n-propoxy, iso-butoxy, sec-butoxy, tert-butoxy, heptoxy, hexoxy, octoxy, dodecoxy, tetracosocy,

fluoro, chloro and bromo groups, X represents any number of $0 < X < 1$, and n represents the degree of polymerization and is 3 or above.)

[Claim 8] A flexible conductive material, which has a transparent conductive polymer film formed by coating the conductive composition comprising a water-soluble conductive polymer (A) having a sulfonic acid group and/or a carboxyl group, a vinyl polymer emulsion (B) with a glass transition temperature of 40°C or below and a solvent (C).

[Claim 9] The flexible conductive material according to Claim 8, wherein the transparent conductive polymer film contains a surfactant (D).

[Claim 10] The flexible conductive material according to Claim 8 or 9, wherein the transparent conductive polymer film contains a polyvinyl alcohol (E).

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention] The present invention relates to a conductive composition and a flexible conductive material formed from the conductive composition. In more detail, the present invention relates to a conductive composition which is satisfactorily applicable to flexible and porous basic mate-

rials, has a high flexibility for keeping conductivity without destructing the resultant conductive material due to expansion/shrinkage of basic material, excellent stability during blending and storage and can form a conductive material having transparency, smoothness and conductivity and a flexible conductive material using the same.

[0002] The conductive composition of present invention is applicable to various anti-static agents, condenser, battery, EMI shield, chemical sensor, display element, nonlinear material, anticorrosive, adhesive, fiber, anti-static coating, improvement on storage capacity of battery, etc. Particularly, the application of the conductive material obtained from the conductive composition of present invention to anti-static agent of a flexible basic material because it has less humidity-dependence of conductivity and high flexibility. As specific uses as anti-static agent, packaging material, magnetic card, magnetic tape, photographic film, printing material, conductive roll, release film, heat seal tape/film, IC tray, IC carrier tape and cover tape, etc. are given.

[0003]

[Prior Art] As means for eliminating electrostatic trouble to plastics, a method for imparting conductivity to plastics with a conductive primer and an antistatic agent, etc. has

generally been used. 7,7,8,8-tetracyanoquinodimethane (TCNQ) complex salts, conductive polymers such as polyaniline, etc., metallic powders and carbon powder, conductive ingredient using surfactants, combinations of these ingredients and polymeric compounds have been known as conductive components. Conductive materials given by forming a conducting film on a basic material with a conductive coating composed of the composition have been known as conductive materials. For example, a conductive filler or a conductive additive is added into a primer to make the surface of a non-conductive material to be conductive with a conductive primer.

[0004] Conductive primer compositions using conductive carbon, silver, nickel, aluminum, etc. for plastics (Japan Kokai 58-76266, Japan Kokai 61-218639, Japan Kokai 02-120373, Japan Kokai 02-194071) have been specifically proposed as conductive fillers, but these conductive primer compositions for plastics disperse the conductive fillers, therefore it is feared that the conductive fillers and resin components separate and agglomerate during storage and have a drawback that the storage stability is

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said to be bad. The conductive primers using these conductive fillers are generally expensive, the film must also be thickened

to obtain necessary conductivity in practical uses, therefore they have a problem with cost in the industry.

[0005] A method for using low-priced surfactants as additives for imparting the conductivity has also been proposed (Japan Kokai 03-4970), but it has such problems that the conductivity changes with environment, particularly, the conductivity markedly lowers in an environment of low humidity. Many currently used conductive primers and anti-static agents are organic solvents, thus the replacement with aqueous systems is wanted from problems of environment, safety, etc.

[0006] To solve these problems, the inventors designed a conductive coating resin composition (Japan Kokai 11-185523). The composition is an aqueous conductive composition comprising a water-soluble conductive polymer, and a conductive composition having satisfactory blending stability, conductivity and transparency is obtained by using specific nonionic surfactants. However, when the composition is coated on a porous and flexible basic material like a resin foam, cracks occur on a formed conductive film due to expansion/shrinkage of basic material, a conducting path is cut off and thus the conductivity disappears, therefore a conductive composition applicable to a flexible basic material and capable of forming a flexible conductive material with satisfactory adhesion has been desired.

[0007]

[Problem to Be Solved by the Invention] The purpose of present invention consists in providing a conductive composition which has satisfactory flexibility, excellent stability during blending and storage, forms a conductive material having satisfactory transparency, smoothness and conductivity, etc., particularly, does not lower the conductivity due to cracks even if a flexible basic material, such as elastomer, etc., expands and shrinks after the conductive material is formed on the basic material.

[0008]

[Means for Solving the Problems] The inventors made earnest study on a conductive composition which should solve these problems of prior art, consequently they discovered that a conductive composition suited to flexible basic materials is obtained by combining a water-soluble conductive polymer of specific structure and a vinyl polymer of specific physical properties and thus came to accomplish this invention.

[0009] Namely, the first invention consists in a conductive composition which comprises a water-soluble conductive polymer (A) having a sulfonic acid group and/or a carboxyl group, a vinyl polymer emulsion (B) with a glass transition temperature of 40°C or below and a solvent (C). The second invention consists

in a flexible conductive material having a transparent conductive polymer film formed by coating a conductive composition comprising a water-soluble conductive polymer (A) having a sulfonic acid group and/or a carboxyl group, a vinyl polymer emulsion (B) with a glass transition temperature of 40°C or below and a solvent (C) on a basic material.

[0010]

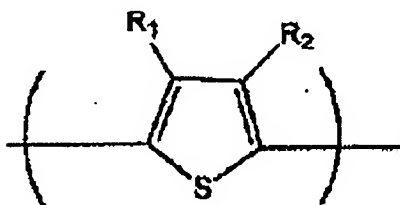
[Embodiment of the Invention] The invented conductive composition and the flexible conductive material are described in detail below. The water-soluble conductive polymers (A) are not specially limited if it is a water-soluble conductive polymers having a sulfonic acid group and/or a hydroxyl group, more specifically, water-soluble conductive polymers shown in Japan Kokai 61-197633, Japan Kokai 63-39916, Japan Kokai 01-301714, Japan Kokai 04-268331, Japan Kokai 04-32848, Japan Kokai 04-328181, Japan Kokai 06-145386, Japan Kokai 05-504153, Japan Kokai 05-503953, Japan Kokai 06-56987, Japan Kokai 05-226238, Japan Kokai 05-178989, Japan Kokai 06-293828, Japan Kokai 07-118524, Japan Kokai 06-32845, Japan Kokai 06-87949, Japan Kokai 06-256516, Japan Kokai 07-41756, Japan Kokai 07-48436, etc. are preferably used.

[0011] As soluble conductive polymers (A), more specifically, water-soluble conductive polymers which contain at least one

or more repeating units selected from a set composed of unsubstituted and substituted phenylenevinylene, vinylene, thienyl, pyrrolylene, phenylene, iminophenylene, isothianaphthene, furylene and carbazolyene, etc. and has a sulfonic acid group or carboxyl group, an alkyl substituted by a sulfonic acid group or carboxyl group or an alkyl group containing an ether bond on the skeleton of a π -conjugated polymer or a nitrogen atom of the polymer are given. Water-soluble conductive polymers having a skeleton containing thienylene, pyrrolylene, iminophenylene, phenylenevinylene, carbazolyene, isothianaphthene are more preferable used among them.

[0012] The conductive composition according to any of Claims 1 ~ 4, wherein a preferable water-soluble conductive polymer (A) contains 20 ~ 100% of at least one repeating unit selected from a set composed of

[Chem 8]

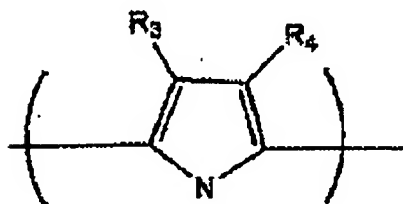


(where R_1 , R_2 are selected from a set composed of H, $-\text{SO}_3^-$, $-\text{SO}_3\text{H}$, $-\text{R}_{35}\text{SO}_3^-$, $-\text{R}_{35}\text{SO}_3\text{H}$, $-\text{OCH}_3$, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{N}(\text{R}_{35})_2$, $-\text{NH}-\text{COR}_{35}$, $-\text{OH}$, $-\text{O}-$, $-\text{SR}_{35}$, $-\text{OR}_{35}$, $-\text{OCOR}_{35}$, $-\text{NO}_2$, $-\text{COO}^-$, $-\text{R}_{35}\text{COO}^-$, $-\text{COOH}$,

$-R_{35}COOH$, $-COOR_{35}$, $-COR_{35}$, $-CHO$ and $-CN$, respectively and separately; here, R_{35} is a $C_1 \sim C_{24}$ alkyl, aryl or aralkyl or alkylene, arylene or aralkylene group, and at least one of R_1 , R_2 is a group selected from a set composed of $-SO_3^-$, $-SO_3H$, $-R_{35}SO_3^-$, $-R_{35}SO_3H$, $-COOH$, $-COO^-$, $-R_{35}COO^-$ and $-R_{35}COOH$.)

[0013]

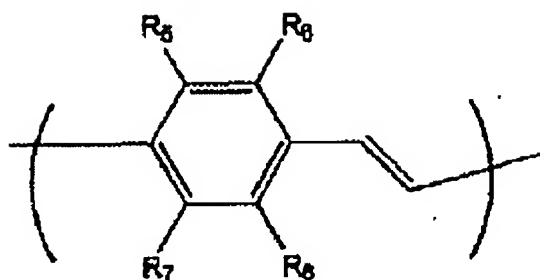
[Chem 9]



(where R_3 , R_4 are selected from a set composed of H , $-SO_3^-$, $-SO_3H$, $-R_{35}SO_3^-$, $-R_{35}SO_3H$, $-OCH_3$, $-CH_3$, $-C_2H_5$, $-F$, $-Cl$, $-Br$, $-I$, $-N(R_{35})_2$, $-NHCOR_{35}$, $-OH$, $-O^-$, $-SR_{35}$, $-OR_{35}$, $-OCOR_{35}$, $-NO_2$, $-COO^-$, $-R_{35}COO^-$, $-COOH$, $-R_{35}COOH$, $-COOR_{35}$, $-COR_{35}$, $-CHO$ and $-CN$, respectively and separately; here, R_{35} is a $C_1 \sim C_{24}$ alkyl, aryl or aralkyl or alkylene, arylene or aralkylene group, and at least one of R_3 , R_4 is a group selected from a set composed of $-SO_3^-$, $-SO_3H$, $-R_{35}SO_3^-$, $-R_{35}SO_3H$, $-COOH$, $-COO^-$, $-R_{35}COO^-$ and $-R_{35}COOH$.)

[0014]

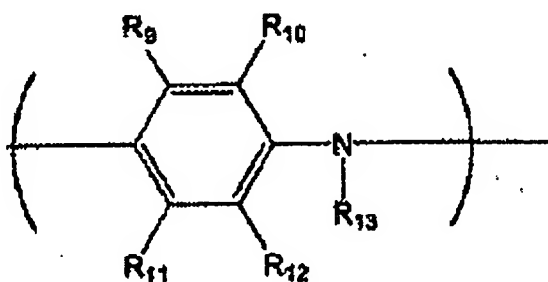
[Chem 10]



(where $R_5 \sim R_8$ are selected from a set composed of H, $-\text{SO}_3^-$, $-\text{SO}_3\text{H}$, $-\text{R}_{35}\text{SO}_3^-$, $-\text{R}_{35}\text{SO}_3\text{H}$, $-\text{OCH}_3$, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{N}(\text{R}_{35})_2$, $-\text{NH}-\text{COR}_{35}$, $-\text{OH}$, $-\text{O}^-$, $-\text{SR}_{35}$, $-\text{OR}_{35}$, $-\text{OCOR}_{35}$, $-\text{NO}_2$, $-\text{COO}^-$, $-\text{R}_{35}\text{COO}^-$, $-\text{COOH}$, $-\text{R}_{35}\text{COOH}$, $-\text{COOR}_{35}$, $-\text{COR}_{35}$, $-\text{CHO}$ and $-\text{CN}$, respectively and separately; here, R_{35} is a $\text{C}_1 \sim \text{C}_{24}$ alkyl, aryl or aralkyl or alkylene, arylene or aralkylene group, and at least one of $R_5 \sim R_8$ is a group selected from a set composed of $-\text{SO}_3^-$, $-\text{SO}_3\text{H}$, $-\text{R}_{35}\text{SO}_3^-$, $-\text{R}_{35}\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{COO}^-$, $-\text{R}_{35}\text{COO}^-$ and $-\text{R}_{35}\text{COOH}$.)

[0015]

[Chem 11]



(where $R_9 \sim R_{13}$ are selected from a set composed of H, $-\text{SO}_3^-$, $-\text{SO}_3\text{H}$, $-\text{R}_{35}\text{SO}_3^-$, $-\text{R}_{35}\text{SO}_3\text{H}$, $-\text{OCH}_3$, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$,

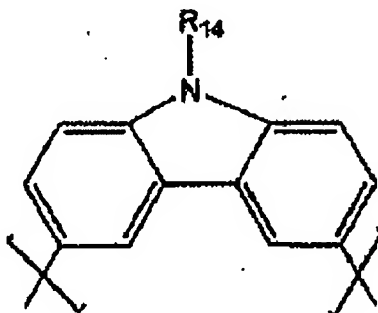
-N(R₃₅)₂, -NHCOR₃₅, -OH, -O⁻, -SR₃₅, -OR₃₅, -OCOR₃₅, -NO₂, -COO⁻,
-R₃₅COO⁻, -COOH, -R₃₅COOH, -COOR₃₅, -COR₃₅, -CHO and -CN, respec-
tively and separately; here, R₃₅ is a C₁ ~ C₂₄ alkyl, aryl or aral-

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kyl or alkylene, arylene or aralkylene group, and at least one
of R₉ ~ R₁₃ is a group selected from a set composed of -SO₃⁻, -
SO₃H, -R₃₅SO₃⁻, -R₃₅SO₃H, -COOH, -COO⁻, -R₃₅COO⁻ and -R₃₅COOH.)

[0016]

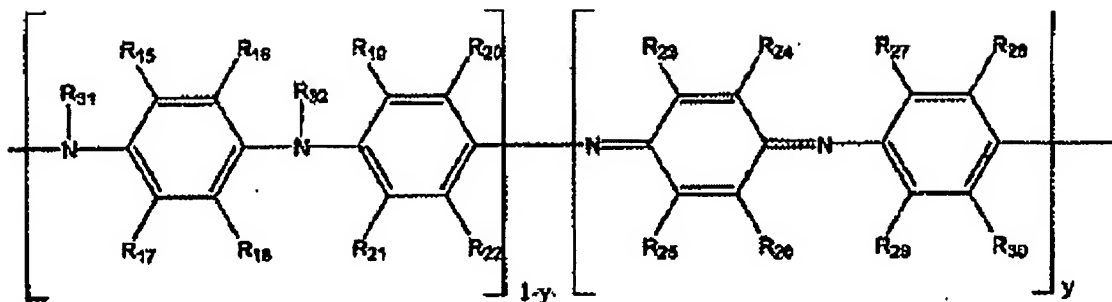
[Chem 12]



(where R₁₄ is selected from a set composed of -SO₃⁻, -SO₃H, -R₃₆-
SO₃⁻, -R₃₆SO₃H, -COOH, -COO⁻, -R₃₅COO⁻, -R₃₅COOH; here, R₃₆ is a C₁ ~
C₂₄ alkylene, arylene or aralkylene group.) in all repeating
units of polymer and has a molecular weight of 2,000 ~
1,000,000.

[0017] In the above conductive compositions, the water-
soluble conductive polymer (A) containing 20 ~ 100% of repeating
units expressed by the following general formula (6)

[Chem 13]



(where y represents any number of $0 < y < 1$, $R_{15} \sim R_{32}$ are selected from a set composed of H, $-\text{SO}_3^-$, $-\text{SO}_3\text{H}$, $-\text{R}_{35}\text{SO}_3^-$, $-\text{R}_{35}\text{SO}_3\text{H}$, $-\text{OCH}_3$, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{N}(\text{R}_{35})_2$, $-\text{NHCOR}_{35}$, $-\text{OH}$, $-\text{O}-$, $-\text{SR}_{35}$, $-\text{OR}_{35}$, $-\text{OCOR}_{35}$, $-\text{NO}_2$, $-\text{COO}^-$, $-\text{R}_{35}\text{COO}^-$, $-\text{COOH}$, $-\text{R}_{35}\text{COOH}$, $-\text{COOR}_{35}$, $-\text{COR}_{35}$, $-\text{CHO}$ and $-\text{CN}$, respectively and separately; here, R_{35} is a $\text{C}_1 \sim \text{C}_{24}$ alkyl, aryl or aralkyl or alkylene, arylene or aralkylene group, and at least one of $R_{15} \sim R_{32}$ is a group selected from a set composed of $-\text{SO}_3^-$, $-\text{SO}_3\text{H}$, $-\text{R}_{35}\text{SO}_3^-$, $-\text{R}_{35}\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{COO}^-$, $-\text{R}_{35}\text{COO}^-$ and $-\text{R}_{35}\text{COOH}$.) in all repeating units of polymer is preferably used.

[0018] Here, the water-soluble conductive composition whose content of sulfonic acid group and carboxyl group to the total number of aromatic rings is 50% or above, preferably 70% or above, more preferably 90% or above, and especially preferably 100% is used because the solubility is very satisfactory.

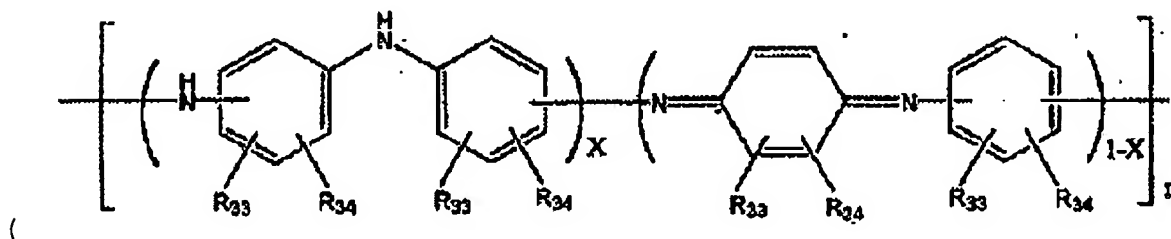
[0019] Substituents attached to aromatic rings are preferably electron-donating groups from viewpoints of conductivity

and solubility, more specifically, soluble conductive polymers having alkyl, alkoxyl groups, halogen atoms, preferably alkoxyl groups are the most preferable.

[0020] Water-soluble conductive polymers expressed by the following general formula (7) are most preferably used in these combinations.

[Chem 14]

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(where R_{33} represents one group selected from a set composed of a sulfonic acid group, a carboxyl group, their alkali metal salts, ammonium salts and substituted ammonium salts, R_{34} represents one group selected from a set composed of methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, dodecyl, tetracosyl, methoxy, ethoxy, n-propoxy, iso-butoxy, sec-butoxy, tert-butoxy, heptoxy, hexoxy, octoxy, dodecoxy, tetracosocyl, fluoro, chloro and bromo group, X represents any number of $0 < X < 1$, and n represents the degree of polymerization and is 3 or above.)

[0021] Known methods may be used as methods for preparing water-soluble conductive polymers (A) and are not specially limited. For example, polymerizable monomers such as heterocyclic compounds having skeletons of thienylene, pyrrolylene, iminophenylene, etc., polymers obtained by polymerizing aniline compounds, etc. according to various synthetic methods such as chemical oxidation process, electrolytic oxidation process, etc. can be used. For example, synthetic methods proposed by the inventors and described in Japan Kokai 07-196791, 07-324132 are suitably used.

[0022] It is desirable that at least a part of acid groups contained in the water-soluble conductive polymers (A) used in the present invention is free acid type from a viewpoint of improving the conductivity. The water-soluble conductive polymers (A) with a mass-average molecular weight of 2,000 or above, preferably 3,000 ~ 1,000,000 and more preferably 5,000 ~ 500,000 by polyethylene glycol conversion of GPC used in the present invention has excellent film-forming property and film strength and is preferably used. Here, polymers with a mass-average molecular weight of under 2,000 is excellent in solubility but insufficient in conductivity and film-forming property; polymers with a mass-average molecular weight of over 1,000,000 is excellent in conductivity but insufficient in solubility.

[0023] The vinyl polymer emulsions (B) used in the present invention are not specially limited if the glass transition temperature of polymers is 40°C or below, for example, polymers or copolymers with a glass transition temperature of 40°C or below, which contain one or more of monomers selected from vinyl polymerizable monomers (called vinyl polymerizable monomers (G) hereafter): alkyl methacrylates such as methyl methacrylate, ethyl meth-acrylate, n-butyl methacrylate, i-butyl methacrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, n-lauryl methacrylate, n-stearyl methacrylate, cyclohexyl methacrylate, etc.; alkyl acrylates such as methyl acrylate, ethyl acrylate, n-butyl acrylate, i-butyl acrylate, t-butyl acrylate, 2-ethylhexyl acrylate, n-lauryl acrylate, n-stearyl acrylate, cyclohexyl acrylate, etc.; hydroxyalkyl methacrylates such as 2-hydroxy-ethyl methacrylate, 4-hydroxybutyl methacrylate, 6-hydroxyhexyl methacrylate, etc.; hydroxyalkyl acrylates such as 2-hydroxy-ethyl acrylate, 4-hydroxybutyl acrylate, 6-hydroxyhexyl acrylate, etc.; glycidyl-containing vinyl polymerizable monomers such as glycidyl methacrylate, glycidyl acrylate, etc.; aromatic vinyl polymerizable monomers such as styrene, α -methylstyrene, etc.; amido-containing vinyl monomers such as methacrylamido, acrylamido, diacetone-acrylamido group, etc.; carboxyl-containing vinyl polymerizable monomers such as

methacrylic acid, acrylic acid, itaconic acid, crotonic acid, fumaric acid, maleic acid, sorbic acid, etc.; nitrile grouping-containing vinyl polymerizable monomers such as acrylonitrile, etc. are used.

[0024] A measured value or a value calculated by a computing equation such as Fox's equation, etc. can be used as the glass transition temperature in the present invention. The glass transition temperature of polymers of the vinyl polymer emulsions in the present invention is 40°C or below, preferably 15°C or below. Here, if the glass transition temperature is over 40°C, the flexibility of resultant conductive material markedly reduces, when a conductive material is formed on a soft and porous basic material like elastomer, the conductive material cracks and the conducting path is cut off due to the expansion/shrinkage of the basic material, therefore the conductivity disappears. The lower limit of glass transition temperature of polymers is preferably -10°C or above.

[0025] As methods for preparing the vinyl polymer emulsions (B) used in the present invention, they are not specially limited, for example, a method for emulsion dispersing a vinyl polymer synthesized by solution polymerization, etc. in a solvent, a method for emulsion polymerization of a vinyl polymerizable monomer (G), etc. are given, if the productivity of

conductive composition is considered, one prepared by emulsion polymerization is preferable among them. Moreover, as the above emulsion polymerization methods, a method for emulsion polymerization of a vinyl polymerizable monomer (G) in a solvent wherein an acid group-containing vinyl polymer (F) obtained by suspension polymerization process is dissolved or dispersed with a basic

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compound is more preferable.

[0026] As solvents for the above emulsion polymerization, they are not specially limited, water or mixed systems of water and alcohols such as methanol, ethanol, isopropyl alcohol, propyl alcohol, butanol, etc.; ketones such as acetone, ethyl isopropyl ketones, ethylene glycols such as ethylene glycol, ethylene glycol methyl ether, etc.; propylene glycols such as propylene glycol, propylene glycol butyl ether, propylene glycol propyl ether, etc.; amides such as dimethylformamide, dimethylacetamide, etc.; or pyrrolidones such as N-methylpyrrolidone, N-ethylpyrrolidone, etc. are preferably used. When the mixed systems of water are used, water/organic solvent is preferably 1/100 ~ 100/1 (mass ratio).

[0027] The acid group-containing vinyl polymer (F) are constructed by one or more monomers selected from acid group-containing vinyl polymerizable monomers such as methacrylic

acid, acrylic acid, crotonic acid, itaconic acid, etc. and one or more of monomers containing vinyl polymerizable monomers (G). The solid acid value of the acid group-containing vinyl polymers (F) is preferably 50 ~ 200 mgKOH/g, more preferably 70 ~ 150 mgKOH/g, and the balance of solubility and water resistance, moisture resistance becomes especially satisfactory. If the solid acid value is less than 50 mgKOH/g, the acid group-containing vinyl polymer (I) is hard to dissolve or disperse in a solvent (C) with a basic compound; if it is more than 200 mgKOH/g, the dispersion stability in suspension polymerization lowers and the water resistance, moisture resistance and adhesion to basic material of obtained conductive material reduce.

[0028] The mass average molecular weight of acid group-containing vinyl polymer (F) is preferably 5,000 ~ 50,000, more preferably 8,000 ~ 40,000. If the mass average molecular weight is under 5,000, the dispersion stability in suspension polymerization lowers; if it is over 50,000, the dispersion and dissolution of acid group-containing vinyl polymer (F) in a solvent with a basic compound becomes difficult.

[0029] The solution polymerization or emulsion polymerization in preparation of vinyl polymer emulsion (B) can be carried out under well-known polymerization conditions with well-known radical polymerization initiators. As radical polymerization ini-

tiators, more specifically, azo compounds such as azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile), etc.; inorganic peroxides such as ammonium persulfate, potassium persulfate, etc., organic peroxides such as benzoyl peroxide, t-butyl hydroperoxide, di-t-butylperoxide, cumene hydroperoxide, etc.; redox catalysts represented by combinations of potassium peroxide or ammonium peroxide and sodium hydrogen sulfite or rongalite; combinations of organic peroxides such as t-butyl hydroperoxide or cumene hydroperoxide, etc. and sodium hydrogen sulfate or rongalite; etc. are given.

[0030] The amount of above radical polymerization initiators is commonly in a range of 0.01 ~ 10 mass% to the total amount of vinyl polymerizable monomers (G) and, if the progress of polymerization and the control of reaction is taken into consideration, it is preferably in a range of 0.1 ~ 5 mass%. Chelating agents such as compounds containing a divalent iron ion such as ferric sulfonate and disodium ethylenediamine tetraacetate, etc. can be used for imparting activity of polymerization initiators.

[0031] In the emulsion polymerization, well-known surfactants and chain transfer agents can be used if necessary. As surfactants, for example, anionic surfactants such as sodium dodecyl benzene sulfonate, sodium lauryl sulfonate, sodium

lauryl sulfate, etc.; nonionic surfactants containing polyoxyethylene group, polyoxyethylene nonylphenyl ether, polyoxyethylene lauryl ether, etc.; reactive surfactants having a vinyl polymerizable double bond, etc. are given. As chain transfer agents, for example, mercaptans such as n-dodecylmercaptan, n-octylmercaptan, n-tetradecylmercaptan, n-hexylmercaptan, etc.; halogen compounds such as carbon tetrachloride, ethylene bromide, etc. can be given.

[0032] Methods for charging vinyl polymerizable monomers (G) in the emulsion polymerization are not specially limited, and any methods such as batch charging method, dropping method, a method wherein a part of vinyl polymerizable monomers (G) are charged in a reactor and the rest is dropped may be used. When a vinyl polymerizable monomer is dropped, a monomer may be dropped into an aqueous solution of surfactant in a reactor as it is, and a surfactant is added into the dropping solution, preliminarily emulsified and then dropped into a reactor. When an acid component such as acrylic acid, etc. is used, the storage stability of emulsion can also be enhanced by neutralization after the end of emulsion polymerization.

[0033] The acid group-containing vinyl polymers (F) are prepared under well known polymerization conditions by using well known initiators, dispersants, chain transfer agents. As

specific examples of initiators, for example, azo compounds such as azobisisobutyronitrile, 2,2'-azobis((2,4-dimethylvaleronitrile), etc.; organic peroxides such as benzoyl peroxide, etc. are given. As specific examples of chain transfer agents, mercaptans such as n-dodecylmercaptan, n-octylmercaptan, n-tetradecylmercaptan, n-hexylmercaptan, etc. are given.

[0034] As basic compounds for dissolving and dispersing the acid group-containing vinyl polymers (F) in solvents, they are not specially limited, for example, ammonia, triethylamine, tri-

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propylamine, etc. are preferably used. The amount of basic compounds is preferably in a range of 0.5 ~ 1 eq. to the acid group in the acid group-containing vinyl polymers (F). If the amount is less than 0.5 eq., the acid group-containing vinyl polymers (F) are hard to dissolve in solvents; if it is more than 1 eq., the emulsion polymerization stability of vinyl polymerizable monomers (G) becomes inferior.

[0035] The amount of vinyl polymerizable monomers (G) to acid group-containing vinyl polymers (F) is preferably in a range of 50 ~ 300 mass parts to 100 mass parts of acid group-containing vinyl polymers (F). If the amount is less than 50 mass parts, the conductivity of conductive material obtained from the invented conductive composition is easy to be impaired.

If it is more than 300 mass parts, the emulsion polymerization stability of vinyl polymerizable monomers (G) becomes inferior.

[0036] As solvents (C) used in the present invention, water, or mixed systems of water and alcohols such as methanol, ethanol, isopropyl alcohol, propyl alcohol, butanol, etc.; ketones such as acetone, ethyl isopropyl ketones, etc.; ethylene glycols such as ethylene glycol, ethylene glycol methyl ether, etc.; propylene glycols such as propylene glycol, propylene glycol butyl ether, propylene glycol propyl ether, etc.; amides such as dimethylformamide, dimethylacetamide, etc.; or pyrrolidones such as N-methylpyrrolidone, N-ethylpyrrolidone, etc. are preferably used. When the mixed systems of water are used, water/organic solvent is preferably 1/100 ~ 100/1 (mass ratio).

[0037] As surfactant (D) used in the invention, surfactants such as anionic surfactants, nonionic surfactants, cationic surfactants, etc. are used, nonionic surfactants are preferably used, and nonionic surfactants with HLB of 16 or over are more preferably used because they improve the stability during blending and storage of conductive composition and improve the appearance of obtained conductive material. The upper limit of HLB is preferably 30 or below from practical use. HLB is an abbreviation of hydrophile-lipophile balance, and it is an indication exhibiting the hydrophilicity of surfactants, etc.

[0038] As specific examples of the above nonionic surfactants with HLB of 16 or over, polyoxyethylene alkyl phenyl ethers with HLB of 16 or over, polyoxyethylene alkyl ethers with HLB of 16 or over, etc. are given. Polyoxyethylene alkyl phenyl ethers with HLB of 16 or over are more preferable among them for obtaining the stability during blending and storage and the effect of improving the appearance of conductive material in a smaller amount.

[0039] The polyvinyl alcohols (E) used in the present invention are not specially limited if they are common polyvinyl alcohols, but modified polyvinyl alcohols having an alkyl group at the end are more preferably used, and they enhance the stability during blending of conductive composition and improve the appearance of obtained conductive material.

[0040] The modified polyvinyl alcohols having an alkyl group at the end are not specially limited if they are polyvinyl alcohols in which an alkyl group is introduced at the end, but polyvinyl alcohols having a carbon number of 3 ~ 20 of end alkyl group, 100 ~ 1,000 repeating units of main chain thereof and a degree of suspension of 85 ~ 100% are more preferable for obtaining the stability during blending and storage and the effect of improving the appearance of conductive material in a smaller amount.

[0041] These surfactants (D) and polyvinyl alcohols (E) give the effects even they are used in the conductive composition, respectively and separately, but they show a larger effect of improving the stability during blending the conductive composition by using them together.

[0042] Next, methods for blending the invented conductive composition are specifically described. The blending method of the invented conductive composition are not specially limited, for example, a method wherein a vinyl polymer emulsion (B) is added into a solvent (C) and then a powder or a solution of a water-soluble conductive composition (A) is added, or a method wherein a powder or a solution of a soluble conductive polymer (A) is added into a vinyl polymer emulsion (B) containing a surfactant (D) and/or a polyvinyl alcohol (E) and a solvent (C), etc. beforehand are given.

[0043] Methods of adding a polyvinyl alcohol (E) into a vinyl polymer emulsion (B) are also not specially limited, and the surfactant (D) may be added as a surfactant for emulsion polymerization in the preparation of vinyl polymer emulsion (B) or may be added at the end of emulsion polymerization.

[0044] Similarly, Methods of adding a surfactant (D) into a vinyl polymer emulsion (B) are not specially limited, and the polyvinyl alcohol (E) may be added as a surfactant for emulsion

polymerization in the preparation of vinyl polymer emulsion (B) or may be added at the end of emulsion polymerization.

[0045] The water-soluble conductive composition (A) and the vinyl polymer in the vinyl polymer emulsion (B) used in the present invention are added so that the ratio (a)/(b) of the mass (a) of (A) to the mass (b) of vinyl polymer in (B) is preferably in a range of 0.05 ~ 4, more preferably in a range of 0.01 ~ 3. If the (a)/(b) is less than 0.05, the conductivity of conductive material becomes inferior; if it is more than 4, the stability during blending and storage of conductive composition deteriorates and the water resistance, moisture resistance of obtained conductive material reduce.

[0046] The water-soluble conductive composition (A) and the solvent (C) used in the present invention are added so that the ratio (a)/(c) of the mass (a) of (A) to the mass (c) of solvent (C) is preferably in a range of 0.0001 ~ 5. If the ratio (a)/(c) is less than 0.0001, the conductivity of conductive material

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becomes inferior; if it is more than 5, the stability during blending and storage of conductive composition deteriorates and the water resistance, moisture resistance, smoothness of obtained conductive material reduce.

[0047] The surfactant (D) and the vinyl polymer of vinyl polymer emulsion (B) used in the present invention are added so that the ratio $(d)/(b)$ of the mass (d) of (D) to the mass (b) of vinyl polymer in (B) is preferably in a range of 0.001 ~ 0.1. If the ratio $(d)/(b)$ is less than 0.001, the stability during blending and storage deteriorates and the appearance of obtained conductive material also becomes inferior; if it is more than 0.1, adverse effects are exerted to the water resistance, moisture resistance of the conductive material.

[0048] Similarly, the polyvinyl alcohol (E) and the vinyl polymer of vinyl polymer emulsion (B) used in the present invention are added so that the ratio $(e)/(b)$ of the mass (e) of (E) to the mass (b) of vinyl polymer in (B) is preferably in a range of 0.001 ~ 0.1. If the ratio $(e)/(b)$ is less than 0.001, the stability during blending and storage deteriorates and the appearance of obtained conductive material also becomes inferior; if it is more than 0.1, adverse effects are exerted to the water resistance, moisture resistance of the conductive material. The surfactant (D) and the polyvinyl alcohol (E) are also preferably used together in the range of above amounts.

[0049] As basic materials for coating the conductive composition, polymeric compounds, wood, paper, ceramics and their films, foams, elastomers or glass sheet, etc. are used. As poly-

meric compounds and their films, foam, elastomers, for example, polyethylene, polyvinyl chloride, polypropylene, polystyrene, polyester, ABS resin, methacrylic resin, polybutadiene, polycarbonate, polyacrylate, polyvinylidene fluoride, polyamide, polyimide, polyaramid, polyphenylene sulfide, polyether ether ketone, polyphenylene ether, polyether nitrile, polyamide-imide, polyether sulfone, polysulfone, polyether imide, polybutylene terephthalate and its film, foams, elastomers, etc. are given.

[0050] A transparent conductive polymer film is formed on at least one side of these polymer films, therefore the surface of above films is preferably subjected to corona surface treatment or plasma treatment with the purpose of improving the adhesion of polymer films.

[0051] The conductive composition used for forming the invented conductive material is processed at the surface of basic material by methods used in common coating. For example, coating methods with gravure coater, roller coater, curtain flow coater, spin coater, bar coater, reverse coater, kiss coater, fountain coater, rod coater, air doctor coater, knife coater, blade coater, cast coater, screen coater, etc.; spraying methods such as spray coating, etc.; dipping methods such as dipping, etc. are used. After the conductive composition is processed at the surface of basic material, it may be dried at room tempera-

ture ~ 250°C as necessary. Any methods such as ordinary temperature placement, hot-air drying, vacuum drying, etc. can be selected as drying methods.

[0052] When the conductive composition is coated on a plastic basic material such as polypropylene, etc., it may be used by mixing with an emulsion of other resins such as chlorinated polyolefins or a water-soluble resin for improving the adhesion of conductive material to basic material. Moreover, various additives such as pigment, defoaming agent, film-forming auxiliary, UV absorbent, antioxidant, heat resistance improver, levelling agent, anti-sagging agent, matting agent, antiseptic, etc. may also be contained in the invented conductive composition as necessary.

[0053]

[Actual Examples] The present invention is described in more detail by actual examples. Moreover, [pt] in the actual examples represents [part by mass], and [%] represents [mass%].

[0054] Preparation Example 1 Conductive polymer (A-1)

Synthesis of poly(2-sulfo-5-methoxy-1,4-iminophenylene) (A-1)

100 mmol of 2-aminoanisole-4-sulfonic acid was dissolved by stirring in a 4 mol/L aqueous solution of ammonia at 25°C, and then 100 mmol of an aqueous solution of ammonium peroxy-disulfate was dropped. After the dropping was finished, the mixture

was stirred at 25°C for additional 12 hr, subsequently a reaction product was filtered, washed and then dried to give 15 g of a polymer powder. The volume resistance value of this polymer was 9.0 Ωcm .

[0055] Preparation Example 2 Conductive polymer (A-2)

Synthesis of poly(2-sulfo-1,4-iminophenylene) (A-2)

Poly(2-sulfo-1,4-iminophenylene) was synthesized according to a known method [J. Am. Chem. Soc., 113, 2665 ~ 2666 (1991)]. The sulfonic acid content of obtained polymer was 52% to aromatic rings. The volume resistance value of this polymer was 50 Ωcm .

[0056] Preparation Example 3 Conductive polymer (A-3)

Synthesis of poly(2-sulfopropyl-1,4-iminophenylene) (A-3)

Poly(2-sulfopropyl-1,4-iminophenylene) was synthesized according to a known method [J. Chem. Soc. Commun., 180 (1990)].

[0057] Preparation Example 4 Conductive polymer (A-4)

Synthesis of poly(2-sulfopropyl-2,5-thienylene) (A-4)

Poly(2-sulfopropyl-2,5-thienylene) was synthesized according to a known method [Preprints of 39th Conference of Polymer Society of Japan, 561 (1990)].

[0058] Preparation Example 5 Conductive polymer (A-5)

Synthesis of (2-carbonyl-1,4-iminophenylene) (A-5)

100 mmol of 2-aminoanisole-4-carboxylic acid was dissolved by stirring in a 4 mol/L of aqueous solution of ammonia at 25°C, and then 100 mmol of an aqueous solution of ammonium peroxydisulfate was dropped. After the dropping was finished, the mixture was stirred at 25°C for additional 12 hr, subsequently a reaction product was filtered, washed and then dried to give 10 g of a polymer powder.

[0059] Preparation Example 6 Vinyl polymer emulsion (B-1)

233 pt of deionized water, 3 pt of Adeka Reasoap SE-10N (made by Asahi Denka Kogyo Co.) and 6 pt of Emulgen 985 (nonionic surfactant made by Kao Corp., HLB = 18.9) were charged in a flask fitted with a stirrer, a condenser, a temperature control unit, a dropping pump and a nitrogen inlet tube, then stirred and mixed. 20 pt of 100 pt of a mixture comprising 40 pt of methyl methacrylate (MMA hereafter), 28 pt of n-butyl acrylate (BA hereafter), 2-ethylhexyl acrylate (EHA hereafter) and 2 pt of methacrylic acid (MAA) was further charged and heated to 80°C while stirring, and 0.5 pt of potassium persulfate (KPS hereafter) was added. After they were reacted for 30 min, the remaining 80 pt in the former monomer mixture was dropped and polymerized in 2 hr. After the dropping was finished, it was kept at 80°C for 1 hr to give a vinyl polymer emulsion (B-1). The solid content of obtained emulsion was 32%.

[0060] Preparation Example 7 Vinyl polymer emulsions (B-2 and B-3)

Vinyl polymer emulsions (B-2 and B-3) were obtained by similarly carrying out polymerizations as Preparation Example 6 (B-1) except that the monomer compositions and surfactants were changed as described in Table 1.

[0061] Preparation Example 8 Vinyl polymer emulsion (B-4)

200 pt of deionized water and 3 pt of Adeka Reasoap SE-10N (made by Asahi Denka Kogyo Co.) were charged in a flask fitted with a stirrer, a condenser and a temperature control unit and then completely dissolved. Once the stirring was stopped, 30 pt of MMA, 10 pt of EHA, 44 pt of BA, 16 pt of MAA, 0.5 pt of azobisisobutyronitrile and 5 pt of n-dodecylmercaptan were added and the stirring was started again, after heated to 75°C, the mixture was reacted for 3 hr so that the reaction temperature was kept to 80°C. Subsequently, it was heated to 90°C and kept for 1 hr. A reaction product was filtered with a 80 µm mesh screen and then dried to give a vinyl polymer (I). Properties of obtained vinyl polymer (I) are shown in Table 2.

[0062] 100 pt of the vinyl polymer (I) and 410 pt of deionized water were charged in a flask fitted with a stirrer, a condenser, a temperature control unit, a dropping pump and a nitrogen inlet tube. 10 pt of a 28% ammonia water was added

while stirring, the mixture was continued to stir for 30 min, further heated to 80°C and stirred for 1 hr to give an aqueous solution of vinyl polymer (I). 0.5 pt of KPS was added under nitrogen atmosphere while keeping the temperature to 80°C, then a preemulsion prepared beforehand by stirring a mixture of 20 pt of MMA, 60 pt of BA, 10 pt of glycidyl methacrylate (GMA hereafter), 5 pt of Adeka Reasoap SE-10N (made by Asahi Denka Kogyo Co.) and 50 pt of deionized water was dropped and polymerized in 1 hr. After the dropping was finished, it was kept at 80°C for additional 1 hr to give a vinyl polymer emulsion (B-3). The solid content of obtained emulsion was 31%.

[0063] Preparation Example 9 Vinyl polymer emulsions (B-5 and B-6)

Vinyl polymer emulsions (B-5 and B-6) were obtained by similarly carrying out polymerizations as Preparation Example 8 (B-4) except that the monomer compositions are changed as described in Table 2.

[0064] Actual Examples 1 ~ 5

10 pt of a 10% aqueous solution of water-soluble conductive polymer was added while stirring 30 pt of a vinyl polymer emulsion to give a conductive composition (solid content of conductive polymer/solid content of vinyl polymer \approx 10/90). Properties of obtained vinyl polymer are shown in Table 3.

[0065] Actual Examples 6 ~ 10

Emulgen 985 (nonionic surfactant made by Kao Corp., HLB = 18.9) and/or a modified PVA-MP-103 (a modified PVA made by Kuraray Co.), whose amount is shown in Table 3, were added to 30 pt of a vinyl polymer emulsion, and the mixture was stirred for 1 hr. 10 pt of a 10% aqueous solution of conductive polymer (A-1) (solid of conductive polymer = 1 pt) was further added while stirring to give a conductive composition. Properties of the obtained conductive composition are shown in Table 3.

[0066] Comparison Examples 1 and 3

10 pt of a 10% aqueous solution of conductive polymer (A-1) was added while stirring 30 pt of the vinyl polymer emulsion to give a conductive composition (solid of conductive polymer/solid of vinyl polymer \approx 10/90). Properties of the obtained conductive composition are shown in Table 3.

[0067] Comparison Examples 2 and 4

Emulgen 985 (nonionic surfactant, HLB = 18.9, made by Kao Corp.) and/or a modified PVA MP-103 (a modified PVA made by Kuraray Co.), whose amounts are shown in Table 3, were added to 30 pt of a vinyl polymer emulsion (solid of vinyl polymer \approx 9 pt), and the mixture was stirred for 1 hr. 10 pt of a 10% aqueous solution of conductive polymer (A-2) (solid of conductive polymer \approx 1 pt) was further added while stirring to give a

conductive composition. Properties of the obtained conductive composition are shown in Table 3.

[0068] The estimation of performances in actual examples and comparison examples was made by methods shown below.

(1) Blending stability: The stability just after the blending of a conductive composition was visually estimated.

O no agglutinates

Δ agglutinates generate

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× solidification during addition of aqueous solution of conductive polymer

(2) Appearance of conductive material: A blended conductive composition was coated on a glass sheet with a bar coater, dried at room temperature for 1 hr and then heated at 100°C for 1 hr to prepare a test conductive material of 10 μm in film thickness. The appearance of test conductive material was visually estimated.

O smooth and satisfactory transparency

× irregular surface and opaque

[0069] (3) Conductivity: The surface resistance of a conductive covering surface was measured by two-terminal method with 92Z≡ [MCP-TESTER made by Mitsubishi Chemical Co.].

(4) Flexibility: A blended conductive composition was coated on a foam polyethylene by impregnation and heated at 80°C for 2 hr to prepare test pieces. The conductivity after repeating shrinkage with 1 kg load on test pieces and expansion without load 100 times was measured.

○ no change of conductivity

× conductivity disappears

[0070]

[Table 1]

| | Vinyl Polymer Emulsion | | |
|------------------------------|------------------------|-----|-----|
| | B-1 | B-2 | B-3 |
| MMA | 40 | 43 | 70 |
| BA | 28 | 25 | 28 |
| EHA | 30 | 30 | - |
| MAA | 2 | 2 | 2 |
| Glass transition temperature | 8.4 | 13 | 61 |
| Solid content (%) | 32 | 32 | 32 |

Glass transition temperature of homopolymers:

MMA: 105°C,

BA: -54°C,

EHA: -70°C

MAA: 130°C

[0071]

[Table 2]

| | | Vinyl Polymer Emulsion | | |
|----------------------------------|-----|------------------------|-----|-----|
| | | B-4 | B-5 | B-6 |
| Vinyl polymer (I) | MMA | 30 | 34 | 64 |
| | EHA | 10 | 36 | 10 |
| | BA | 44 | 14 | 10 |
| | MAA | 16 | 15 | 16 |
| Vinyl polymerizable monomer (II) | MMA | 20 | 30 | 50 |
| | BA | 60 | 60 | 40 |
| | GMA | 10 | 10 | 10 |

| | | | |
|--|--------|--------|-------|
| Acid value of vinyl polymer (I) (mgKOH/g) | 104 | 104 | 104 |
| Weight-average molecular weight of vinyl polymer (I) | 10,000 | 10,000 | 9,000 |
| Vinyl polymer T _g | 8.8 | 14.5 | 61 |
| Emulsion solid content (%) | 31 | 30 | 30 |

Glass transition temperature of homopolymers: GMA: 74°C

Acid value: number of mg of potassium hydroxide necessary for neutralizing acid group contained in 1 g of vinyl polymer

Weight-average molecular weight: Weight-average molecular weight on standard polystyrene conversion measured by GPC

[0072]

[Table 3]

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| | Soluble Conduc- tive Polymer | Vinyl Polymer Emulsion | Surfac- tant ^{*1} | Poly- vinyl Alcohol ^{*2} | Blending Stabi- lity | Appear- ance of Conduc- tive Material | Surface Resis- tance (Ω) | Flexibi- lity Estima- tion |
|--------------|---------------------------------------|------------------------------|-------------------------------|---|----------------------------|---|-----------------------------------|-------------------------------------|
| Act. Ex. | | | | | | | | |
| 1 | A-1 | B-1 | - | - | O | O | 1×10 ⁷ | O |
| 2 | A-2 | B-1 | - | - | O | O | 7×10 ⁷ | O |
| 3 | A-3 | B-1 | - | - | O | O | 1×10 ⁷ | O |
| 4 | A-4 | B-1 | - | - | O | O | 2×10 ⁷ | O |
| 5 | A-5 | B-1 | - | - | O | O | 2×10 ⁷ | O |
| 6 | A-1 | B-2 | 0.3 | - | O | O | 3×10 ⁷ | O |
| 7 | A-1 | B-4 | 0.3 | | O | O | 2×10 ⁷ | O |
| 8 | A-1 | B-4 | 0.3 | 0.3 | O | O | 4×10 ⁷ | O |
| 9 | A-1 | B-5 | 0.3 | | O | O | 3×10 ⁷ | O |
| 10 | A-1 | B-5 | 0.3 | 0.1 | O | O | 5×10 ⁷ | O |
| Comp. Ex. | | | | | | | | |
| 1 | A-1 | B-3 | - | - | x | x | unmea- surable | unmea- surable |
| 2 | A-2 | B-3 | 0.8 | - | O | O | 5×10 ⁴ | x |
| 3 | A-1 | B-6 | - | - | x | x | unmea- surable | unmea- surable |
| 4 | A-2 | B-? | 0.3 | 0.1 | O | O | 5×10 ⁴ | x |

*1 Surfactant: a nonionic surfactant made by Kao Corp. (trade-name Emulgen 985, HLB = 18.9)

*2 A modified polyvinyl alcohol: Polyvinyl alcohol made by Kuraray Co. (trade-name MP-103)

The amounts of surfactant and polyvinyl alcohol are the ratio (pt) to 9 pt of solid of vinyl polymer emulsion

[0073]

[Effects of the Invention] The invented conductive composition can form a flexible conductive material having excellent stability during blending and storage and satisfactory transparency, smoothness, conductivity, etc. and gives a flexible conductive material which does not cause conductivity reduction due to cracks even if a flexible basic material expands/shrinks and deforms after the conductive material is formed on the basic material, thus the present invention is very helpful in the industry.